Controlled synthesis & optical properties of II-VI semiconductor nanostructures

Joint Laboratory:

Joint Laboratory of Nano-organic Functional Materials and Devices

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Summary of the project:

II-VI compound semiconductors (zinc chalcogenides: ZnO, ZnS, ZnSe, ZnTe; cadmium chalcogenides: CdS, CdSe, CdTe) have outstanding optical properties, such as direct band gap, high fluorescent yield and large exciton binding energy, which can afford the flexibility to fabricate devices such as light emitting diodes (LED) and photodetectors. However, despite their excellent attributes, II-VI compound semiconductors have not yet been made into practical optoelectronic devices. The main obstacle to fabricate II-VI-based devices is largely associated with the poor material quality arising from the current II-VI wafer fabrication technology.

In this joint project, we utilized nanotechnology to effectively ease or overcome the material difficulty, and have made impact in the following areas:

i) Controlled synthesis and assembly of II-VI nanostructures.

ii) Exploration and investigation of novel optical properties in the synthesized II-VI nanostructures in the nanometer scale.

iii) Exploration and investigation of novel properties and applications of II-VI nanostructures.

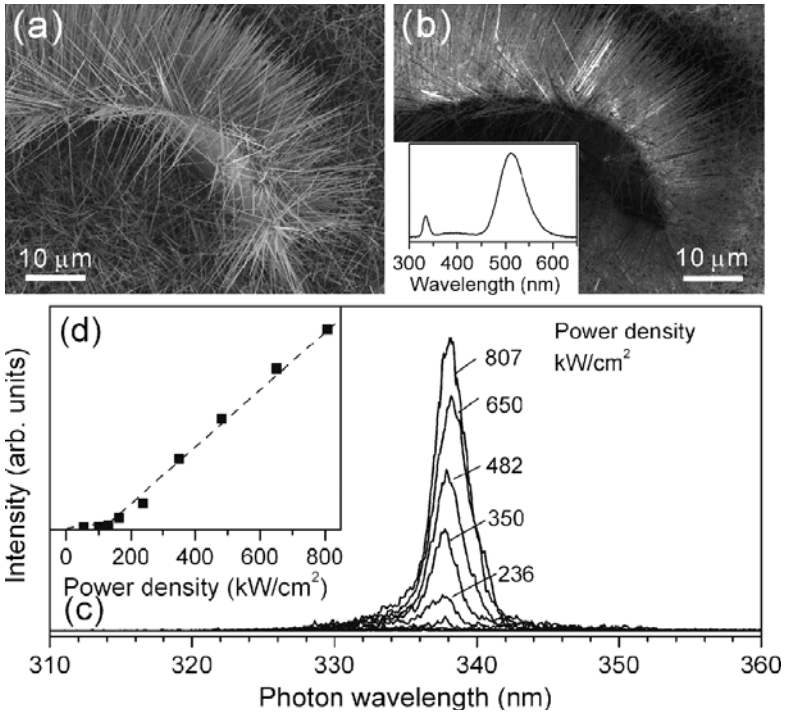
Our results revealed several material advantages of II-VI compound semiconductor nanostructures over their bulk or wafer-size crystal counterparts. Firstly, it is easer to grow nanosized crystals with superior optical qualities with low-defect density. Secondly, II-VI compound semiconductors with different chemical composition can be conveniently integrated into one hierarchical nanostructure. Thirdly, nanostructures of II-VI compound semiconductors can be controllably doped to tailor their optical properties with ease. Based on the new material merits, we achieved significantly enhanced optical properties such as photocurrent and photoluminescence from II-VI compound semiconductor nanostructures. For instance, increase by four orders of magnitude in conductance on light intensity was observed for CdS nanoribbons. The photoresponse speed of a single CdS nanoribbon was much higher (response time hundreds of microseconds) than the conventional film and bulk CdS photodetectors. The findings suggest the great application potential of II-VI compound semiconductor nanostructures in high-sensitivity and high-speed nanoscale devices. Our findings have led to 26 journal articles, and some notable results are listed bellows.

Main publications

1. "Photoresponse Properties of CdSe Single-Nanoribbon Photodetectors", *Advanced Functional Materials* 17, 1795-1800 (2007).
2. "Single-Crystal nanoribbons, nanotubes, and nanowires from intramolecular charge-transfer organic molecules", *J. Amer. Chem. Soc.* 129, 3527-3532 (2007).
3. "Single-crystal organic microtubes with a rectangular cross section", *Angewandte Chemie* 46, 1525-1528 (2007).
4. "Heteroepitaxial growth and optical properties of ZnS nanowire arrays on CdS nanoribbons", *Appl. Phys. Lett.* 90, 093127 (2007).
5. "Facile solution synthesis of hexagonal Alq3 nanorods and their field emission properties", *Chem. Commun* 3083–3085 (2007).
6. "Photoconductive Characteristics of Single-Crystal CdS Nanoribbons", *Nano Lett*. 6(9); 1887-1892 (2006).
7. "Photoluminescence and photoconductivity properties of copper-doped $Cd_{1-x}Zn_xS$ nanoribbons", *Nanotechnology* 17, 5935-5940 (2006).
8. "Dart-shaped tricrystal ZnS nanoribbons", *Angewandte Chemie* 45, 2568-2571 (2006).
9. "Catalyst-assisted formation of nanocantilever arrays on ZnS nanoribbons by post-annealing treatment", *J. Phys. Chem. B.* 110, 6759-6762 (2006).
10. "Gold nanoparticles modified silicon nanowires as biosensor", *Nanotechnology* 17, S276-S279 (2006).
11. "Bulk preparation of $Si–SiO_x$ hierarchical structures: high-density radially oriented amorphous silica nanowires on a single-crystal silicon nanocore", *Angewandte Chemie* 44, 6934-6937 (2005).
12. "Silicon nanowire sensors for bioanalytical applications: glucose and hydrogen peroxide detection", *Adv. Funct. Mater.* 15, 1478-1482 (2005).
13. "Morphology-controllable synthesis of pyrene nanostructures and its morphology dependence of optical properties", *J. Phys. Chem. B* 109, 18777-18780 (2005).
14. "A facile route to fabrication of inorganic–small organic molecule cable-like nanocomposite arrays", *Chem. Commun*. 4202-4204 (2005).
15. "Fabrication and microstructures of Si composite nanocone arrays", *Phys. Stat. Sol. (a)* 202, 2479-2483 (2005).
16. "Morphology-controllable Preparation of 1D Poly (vinyl pyrrolidone) Nanostructured Arrays", *Nanotechnology* 16, 433-436 (2005).
17. "Formation of ZnS/SiO_2 nanocables", *Appl. Phys. Lett*. 86, 173111, (2005)
18. "Sb-induced bicrystal ZnO nanobelts", *Appl. Phys. Lett*. 86, 013103, (2005)
19. "Synthesis and optical properties of Pb-doped ZnO nanowires", *Phys. Stat. Sol. (a)* 202, 405–410 (2005).
20. "Sonochemical synthesis of Single Crystal PbS Nanobelts", *Journal of Solid State Chemistry*, 178 (2005) 399-403.
21. "Preparation and photoluminescence of Sc-doped ZnO nanowires", *Physica E* 25, 587-591 (2005).
22. "Wet chemical synthesis of Ag Nanowires Array at room temperature", *Chem. Lett*. 34, 4, 510 (2005).
23. "Strain energy and electronic structures of silicon carbide nanotubes: Density functional calculations", *Phys. Rev. B* 71, 085312 (2005)
24. "Signature of Nanodiamond in Raman Spectra: A Density Functional Theoretical Study", *J. Phys. Chem. B.* 109, 9006-9013 (2005).
25. "Silicon monoxide clusters: The favorable precursors for forming silicon nanostructures", *Phys. Rev. Lett.* 93, 095503 (2004).
26. "Electrical transport and electronic delocalization of small fullerenes", *J. Phys. Chem. B*. 108, 16636-16641 (2004).

Selected photographs and results:

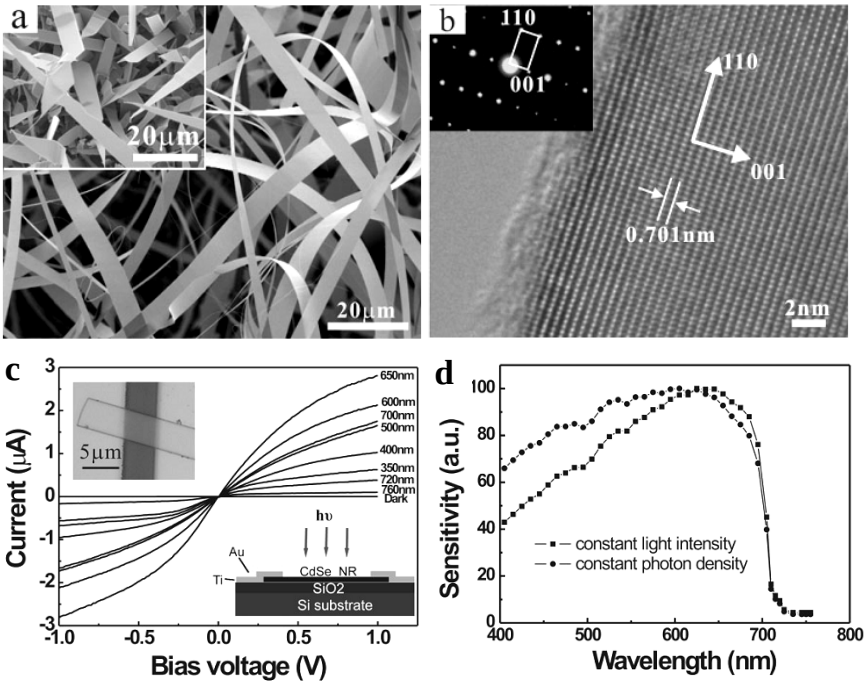
1.



(a) SEM and (b) CL images of ZnS nanowire arrays on CdS nanoribbons. The inset is the corresponding CL spectrum. (c) PL spectra and (d) PL intensity of epitaxially grown nanostructures excited by different excitation power densities.

(From "Heteroepitaxial growth and optical properties of ZnS nanowire arrays on CdS nanoribbons", *Appl. Phys. Lett.* 90, 093127 (2007))

2.



a) SEM image of as-synthesized CdSe nanoribbons. The tapered ribbons with gold tips observed at the early growth stage (inset) indicate the VLS growth mechanism. b) HRTEM image of a CdSe nanoribbon. The corresponding SAED pattern is shown in the inset. Note that the nanoribbon axis is along the [110] direction. The fringe spacing of 0.701 nm corresponding to the (001) lattice spacing of CdSe is denoted. c) I–V curves of a CdSe individual nanoribbon illuminated with light of different wavelength at an intensity of 4.10 mWcm^{-2}. The insets show the optical microscopy image of a single-nanoribbon device (top) and the schematic diagram of the photoconductive measurement (bottom). d) Spectral response of the nanoribbon showing a cut-off wavelength of ca. 710 nm. The curves represent the response spectra plotted at a constant light intensity (●) and a constant photon density (■), respectively.

(From " Photoresponse Properties of CdSe Single-Nanoribbon Photodetectors", *Advanced Functional Materials* 17, 1795-1800 (2007).)